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A MODEL FOR TWO LAYER ADSORPTION
WITH LATERAL INTERACTIONS

by

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled A MODEL FOR TWO LAYER ADSORPTION WITH LATERAL INTERACTIONS, submitted by Douglas L. Hunter, in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

Various theories of physical adsorption are reviewed. Although some theories which treat mobile adsorption are discussed, the emphasis is on localized adsorption theories. The work of Ballentine and Betts in which the Ising model of ferromagnetism is applied to the problem of localized monolayer adsorption with attractive lateral interactions is examined in some detail. An extension of this in which Ballentine applies the three dimensional Ising model to multilayer adsorption is outlined, and results which show the variation in the location of the critical point with the number of layers are given.

A model for two layer adsorption with attractive lateral interactions is proposed. This model is suggested by the Ising model, but it is more realistic concerning the nature of the second layer sites. It is essentially a two dimensional model in which each adsorption site is considered to be in one of three possible "occupation states." The model is specialized in order to simplify the mathematical treatment. The partition function for the system is expanded as an exact series in both high and low temperature variables. The calculation of the series coefficients

involves the technique of configuration counting. An estimate of the location of the critical point for this system is made.

The work of the thesis is summarized and the possibilities of generalizing the treatment and extending the model to include more layers are discussed.

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Chapter I. Introduction

1.1 Adsorption - Definition and History

When a gas or vapour comes into contact with a solid, the gas may be adsorbed onto the surface of the solid or absorbed into the interior of the solid. Regardless of the type of force or combination of forces, a molecule of gas absorbed into a solid is subject to forces equally in all directions. On the other hand molecules adsorbed onto the surface are subject to unbalanced forces which hold it onto the surface. In effect the solid has a "surface tension" and the presence of the adsorbed molecule reduces the surface area and lowers the surface free energy. Thus adsorption is an exothermic reaction and the so-called heat of adsorption is a physically measurable quantity.

Both absorption and adsorption can take place through either a chemical or physical process. If there is a transfer of electrons between the atoms of the gas and the solid then a new compound is formed the process is said to be chemical ab- or adsorption. If however the forces are of the Van der Waals type, i.e., strictly molecular interaction, then the process is physical. In physical absorption a solid solution is formed. In the process of physical adsorption the adsorbed film behaves in many respects like a two-dimensional liquid. Physical adsorption

may further be subdivided into localized and mobile adsorption. In the former the gas molecules which adhere to the solid surface are essentially bound to fixed adsorption centers, whereas in the latter a thin liquid film is formed and the molecules are free to move within the film. The model which we will propose later in this thesis will be for localized physical adsorption with lateral interactions.

Adsorption was first discovered in 1773 by Scheele who found that charcoal in contact with a gas in some way reduced the amount of gas in the free state. The first person to perform a series of systematic experiments on adsorption was de Saussure (1) who, in 1814, measured the amount of adsorption of various gases on many different adsorbents. Since then large numbers of experiments have measured the adsorption of nearly every conceivable combination of adsorbate (gas) and adsorbent (solid). A great difficulty in the study of adsorption has been that many conflicting results have been reported. The reason for this is that the physical properties of the adsorbent depend so much on the way in which the sample is prepared. Thus samples of the same adsorbent prepared in different laboratories, and sometimes even two samples from the same laboratory, may give far from similar results. It was pointed out later that many of the earlier experiments were performed using samples of adsorbent which already contained a composite layer of adsorbed gas molecules and had not been properly "cleaned". This effectively suppressed the properties of the intended adsorbent.

These factors made it difficult to propose and check a theory of adsorption since there were few consistent experimental results. However in 1911 and 1915 Knudsen (2) showed that if one assumed the dimensions of the apparatus were sufficiently small with respect to the mean free path of the gas molecules, one could do calculations using the kinetic theory of gases. Knudsen's experiments tended to support his theoretical calculations. Since that time various theories have been proposed and we shall discuss them later in this thesis.

1.2 Cooperative Phenomena

We consider the class of statistical mechanical systems whose macroscopic properties are determined primarily by the interactions between the microscopic subsystems. Systems in this class are said to exhibit cooperative phenomena. Other than the Bose gas, all systems which show phase transitions fall into this class. The physical adsorption of molecules which interact laterally is a cooperative phenomenon. This exhibits a phase transition known as critical adsorption, where below a given temperature the number of adsorbed molecules increases sharply at a particular pressure.

The simplest model of cooperative behaviour was proposed in 1925 by Ising (3). In this model Ising assumed

that all subsystems of a cooperative assembly were identical and could be in one of two possible states. He also assumed that the interaction between subsystems was sufficiently short range that all but nearest neighbour interactions could be neglected. Ising applied this model to the problem of ferromagnetism. Since then other researchers have extended the theory and applied it to other cooperative systems. Fowler (4) and Peierls (5) were the first (1936) to apply the two-dimensional Ising model to monolayer adsorption with lateral interactions. However, their solutions made use of two different approximations and, although they obtained a critical point, their results in this region were very distorted.

As recently as 1960 Bumble and Honig (6) used another approximate method (due to Hijmans and de Boer (7)) to solve this same problem. In 1962 Ballentine and Betts (8,9) attacked the problem using exact series expansions and showed that complete adsorption isotherms could be calculated in this way. Ballentine extended the approach to include two or more layers of an Ising model and found estimates of the critical adsorption temperature.

1.3 Reasons for Studying the Adsorption Problem

Ballentine in the introduction to his thesis has outlined the reasons for which this research was started.

Various experimentalists have reported adsorption isotherms which exhibit a critical point. Jura et al (10), Fisher and McMillan (11), and Machin and Ross (12) have all found isotherms with single discontinuities, whereas Singleton and Halsey (13) have found a stepwise isotherm which has two distinct discontinuities. This latter result is for the system krypton on graphitized carbon black.

The work done by Ballentine was very successful in providing isotherms for critical monolayer adsorption. Although his study of the n-layer adsorption problem by direct application of the Ising model is certainly justified for the reasons he states, the model does not seem physically realistic in regard to the nature of the sites for adsorption in the second and higher layers. The model which we will propose here, although exploited hardly at all, will be an improvement in this regard. The Ising model, by its very nature, will show but one critical point regardless of the number of adsorbed layers. Physically, however, for an ideally homogeneous adsorbent one would expect critical adsorption as each layer is filled. This is the way in which Halsey and Singleton interpret their result, and this is also supported by the work of Polley, Schaeffer, and Smith (14) who showed that the larger the crystals in the adsorbent the more step-like the isotherm becomes. A further reason for proposing this model is that if it can be solved

without the restrictions which have been placed on the interaction energies, then it is believed that stepwise isotherms would result -- each layer filling discontinuously as the pressure is increased or the temperature lowered.

1.4 The Contents of the Thesis

In chapter II of this thesis we will survey many of the early and current theories of adsorption, starting with the rather simple approach of Henry's law and Langmuir's isotherm, and continuing on to the popular theory due to Brunauer, Emmett, and Teller and some of the modifications that have been suggested for it. Chapter III will contain an outline of the work done by Ballentine and Betts for both monolayer and n-layer adsorption. A reasonable understanding of their work is recommended, for it was this which suggested the model which is proposed in Chapter IV. We will of necessity specialize the model and from the series expansions for the partition function estimate the critical temperature for the adsorbed system. In the concluding chapter we will compare this result with those obtained from other theories, and also discuss the possibilities which remain for the more general model.

Chapter 2. Other Theories of Adsorption

2.1 Monolayer Adsorption Theories

Among the many theories that have been proposed to explain physical adsorption, the simplest is Henry's Law. It assumes that the amount of gas adsorbed is directly proportional to the equilibrium pressure of the gas. To derive this law theoretically one must assume that the behaviour of the gaseous and adsorbed phases is perfect. This is possible only if both phases are extremely dilute. The linear isotherm which describes the adsorption can be written as

$$v = p \frac{\alpha d}{RT} \frac{\omega_2}{\omega_1} e^{\epsilon/RT}, \quad (2.1)$$

where ϵ is the adsorption potential, α is the fraction of the adsorbent available, d is the thickness of the film, ω_1 and ω_2 are in the same ratio as the internal energies of molecules in the gas and adsorbed phases respectively, and p and v are the equilibrium pressure and the volume adsorbed respectively. Isotherms which appear to be linear have been found experimentally, but they cover only a very small part of the possible pressure range. Since the pressure range is so small, and since more accurate measurements on these same systems now show slight deviations from linearity, it is widely held that this picture is far too simple to be a valid theory for adsorption.

The next theory, in order of ascending sophistication, is that due to Langmuir (15). Although nothing is said about the mechanism of adsorption in Henry's Law, we are able to see that the adsorbed layer is mobile, there being nothing to hold a particular molecule to a particular spot on the surface. On the other hand in Langmuir's theory we assume that the gas molecules are adsorbed onto the solid at definite sites, and that each site is capable of holding only one gas molecule. We must also assume that there is no interaction between the adsorbed molecules. Originally the isotherm equation was derived kinetically by assuming that the gas was in equilibrium with the adsorbed layer. By equating the rate at which the molecules evaporated from the surface to the rate at which they "condensed" onto the surface, Langmuir in 1918 obtained an isotherm of the form

$$\theta = \frac{bp}{1 + bp} \quad (2.2)$$

where θ is the fractional coverage, p the equilibrium pressure, and b a function only of temperature. In 1935 Fowler (16) gave a statistical derivation of equation (2.2). It is interesting to note that for very low pressures (i.e., when both the gaseous and adsorbed phases are very dilute) Langmuir's isotherm reduces to Henry's Law. For the other limiting case when $p \rightarrow \infty$, we find $\theta \rightarrow 1$ or $v \rightarrow v_{\max}$, where

v_{\max} equals the volume of a completely filled monolayer.

This model does not permit any adsorption beyond a monolayer.

Williams (17) and Henry (18) have modified the Langmuir model slightly by considering the case where a gas molecule when adsorbed occupies n adjacent adsorption sites on the lattice. Several others have derived an isotherm for the case where the adsorbed molecule dissociates into n atoms and each atom occupies a site. However these isotherms are not very important in physical adsorption and won't be considered further.

Volmer (19) has treated the case for mobile adsorption, i.e., where the adsorbed molecules are free to move in two dimensions on the surface of the adsorbent. By assuming that the gas was perfect and that the adsorbed phase was a two-dimensional gas obeying the (non-perfect) equation of state

$$\phi(A - N\beta) = NkT,$$

where ϕ is the surface pressure, A the area, and β a constant, Volmer obtained an isotherm of the form

$$\frac{N}{A} = \frac{bp}{1 + b'p}, \quad (2.3)$$

which is similar in form, but not identical, to the Langmuir isotherm (2.2) for localized adsorption.

Fowler (4) in 1936 made a very important contribution to the theory of adsorption when he proposed a model which took into account the attractive lateral interactions between molecules in the adsorbed phase. His model was simply the Ising model of ferromagnetism applied to adsorption. He said that the adsorption was localized and the attraction was constant and sufficiently short range in nature that all but nearest neighbour interactions might be neglected. This model will be dealt with in much greater detail in chapter III.

Since at that time no exact methods of solution were known for the Ising model, Fowler made use of the Bragg-Williams (20) approximation in his solution. The number of nearest neighbour pairs of adsorbed molecules, which is required in the calculation, is in this approximation taken as the average number that would occur for a given coverage if the distribution were random. On this basis Fowler derived the following isotherm equation

$$bp = \frac{\theta}{1 - \theta} e^{-\theta_q V/KT}, \quad (2.4)$$

where θ , p , and b have their usual meaning, $-V$ is the

constant interaction energy between nearest neighbours, and q is the coordination number (or number of n-n pairs per site) for the lattice. The most noteworthy property of this solution is that it exhibits critical adsorption. The specific heat is discontinuous as a function of temperature and the isotherms for temperatures below a critical temperature T_c have discontinuities. For the Bragg-Williams approximation the critical temperature is given by

$$\frac{V}{KT_c} = 1 , \quad (2.5)$$

for a simple quadratic lattice. If one applies the quasi-chemical or Bethe approximation to the problem with lateral interactions (5) one gets a more accurate value of the critical temperature

$$\frac{V}{KT_c} = 2 \ln 2 = 1.3863 . \quad (2.6)$$

We shall see in the next chapter how the critical temperature has been found exactly.

2.2 Two Layer Adsorption with Critical Conditions

The work of Cernuschi (21) and Dube (22) is certainly worthy of mention in this review of earlier adsorption theories. Each of them used a two-layer model in which four adsorbed molecules on adjacent sites (forming a square)

in the first layer constitute a site for the possible adsorption of a molecule onto the second layer. Cernuschi neglected lateral interactions while Dube included them. Both of them found results which indicated that critical adsorption could take place for their models, providing the binding energies satisfied a certain condition.

Cernuschi considered the molecules in the first layer to be bound to the surface by an energy $-\chi_0$, and since there was no interaction all configurations were equally probable. On this basis the average number of available sites in the second layer is $(N_1/M_1)^{M_1}$, where N_1 = the number of molecules in the first layer, and M_1 = the number of sites in the first layer. The molecules in the second layer are bound to the surface with energy $-\delta_0$. After finding the partition function using these assumptions, Cernuschi showed that critical adsorption takes place subject to the conditions

$$\theta_{lc} = \frac{3}{4}, \text{ and } KT_c = \frac{\delta_0 - \chi_0}{0.42}. \quad (2.7)$$

Thus if $\chi_0 > \delta_0$ no critical point exists. θ_{lc} is the critical coverage of the first layer.

Cernuschi gave a brief discussion of part of the effect of an attractive interaction χ_1 on this model. He neglected the effect of the interaction on the existence

of second layer sites, and used the Bragg-Williams approximation to calculate the increased binding energy in the first layer due to the interaction. Cernuschi's results showed that the first layer critical coverage decreased with increasing attractive interaction between molecules, while the critical temperature (for fixed χ_o and δ_o) decreased to a minimum for some value of the interaction ($\chi_1 \approx 3(\delta_o - \chi_o)$) and then increased with increasing χ_1 .

Dube used exactly the same picture of adsorption but did better calculations using the attractive interaction χ_1 . He follows Peierls (5) treatment using the Bethe approximation, rather than the Bragg-Williams method as Fowler did, to calculate the effect of the interaction on increasing the probability of existence of second layer sites. The equations he derived had to be solved numerically for different values of the interaction. He defined the probability of existence of a second layer site as $\theta_4 M_1$. Cernuschi used $\theta_1^4 M_1 = (N_1/M_1)^4 M_1$ for this quantity. Dube showed that for all values of χ_1 corresponding to a non-zero attractive interaction $\theta_4 > \theta_1^4$, except at the end points $\theta_1 = 0$ and $\theta_1 = 1$ where $\theta_4 = \theta_1^4$. Dube then used the Bragg-Williams approximation to set up the partition function for the two-layer adsorbed system. He was then able to find all the critical functions in terms of the

energies δ_0 , χ_0 , χ_1 , and a parameter β which enters in the functional fit of $\theta_4(\theta_1, \chi_1)$ to the numerical results. Dube's results again showed that the necessary condition for critical behaviour was that $\delta_0 > \chi_0$.

Fowler's results, using the Ising model, for monolayer adsorption show that the presence of attractive interactions between adsorbed molecules is sufficient to cause critical adsorption to occur; while according to the model of Cernuschi and Dube critical adsorption will occur in two layer adsorption, whether there is lateral interaction between molecules or not, so long as the second layer molecules are bound more tightly to the surface than those in the first layer.

2.3 Multilayer Adsorption Theories

Much of the early theoretical work in adsorption treated one or possibly two layers of adsorbed molecules, rather than many layers. The reason for this was that most early experimental work was done on charcoal, which is a unique adsorbent in that adsorption onto it rarely occurs beyond a monolayer.

The first theory of multilayer adsorption, known as the potential theory, was introduced in 1914 by Polanyi (23). This theory is still accepted today, largely because

it does not insist on a detailed picture of the physical process involved. It treats a mobile film by considering it to be trapped in the potential gradient of the surface force which decays with the distance away from the surface. The adsorption potential ϵ is the measure of the force on an adsorbed molecule, the adsorption potential being the work required to bring a molecule from the ground state of the gas phase to the point in the film at which it is measured. We denote the volume of the adsorbed film as ϕ . We assume that ϵ is independent of T and thus that the curve $\epsilon = f(\phi)$ is sufficient to describe the buildup of the film. $\epsilon = f(\phi)$ is in essence a potential distribution function and it is known as the characteristic curve. This curve cannot be measured directly from any experimental system. Rather, one must take a "master isotherm", one which is known over a large range of adsorbed volumes, and calculate $f(\phi)$, and then from this curve calculate any other isotherm for the system.

An interesting point about this theory is that for different gas systems being adsorbed onto the same solid one can make all the characteristic curves coincide with one another by writing

$$\epsilon = \beta f(\phi) . \quad (2.8)$$

The factor β is known as the "coefficient of affinity" and is different for each adsorbate. It has been found that the physical property of all the adsorbates which is most closely proportional to β is the molar volume of the adsorbate in the liquid phase. With this knowledge one is able to predict something of the adsorbability of a substance without actually performing any experiments.

In 1938 Brunauer, Emmett, and Teller (24) successfully extended the Langmuir model of localized monolayer adsorption to solve the problem of multilayer adsorption. The BET theory, as it is known, made certain simplifying assumptions that made it possible to treat the problem mathematically. First it is assumed that molecules are adsorbed vertically, a molecule in a given layer serving as a site for a molecule to be adsorbed into the next layer. All interactions between molecules in the film are neglected. One denotes the areas of the surface covered by exactly 0, 1, 2, 3, . . . i , layers of molecules by $s_0, s_1, s_2, s_3, \dots s_i$, and assumes that at equilibrium the rate of condensation on top of the $(i - 1)^{\text{st}}$ layer to form i layers is equal to the rate at which molecules evaporate from the i^{th} layer. The equations which represent this equilibrium are:

$$\begin{aligned}
 a_1 p s_0 &= b_1 s_1 e^{-E_1/RT} \\
 a_2 p s_1 &= b_2 s_2 e^{-E_2/RT} \\
 &\cdot \\
 &\cdot \\
 &\cdot \\
 a_i p s_{i-1} &= b_i s_i e^{-E_i/RT} \tag{2.9}
 \end{aligned}$$

where p is the pressure at equilibrium, E_i is the heat of adsorption in the i^{th} layer, and a_i and b_i are constants.

The total surface area of the adsorbed system is given by

$$A = \sum_{i=0}^{\infty} s_i \tag{2.10}$$

and the total volume adsorbed is given by

$$v = v_o \sum_{i=0}^{\infty} i s_i \tag{2.11}$$

where v_o = the volume/unit area/monolayer.

One can then write the coverage in terms of the number of layers by

$$\frac{v}{v_m} = \frac{v}{A v_o} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} \tag{2.12}$$

where v_m is the volume of one complete monolayer.

The assumptions made by Brunauer, Emmett and Teller which effected the solution were that

$$E_2 = E_3 = E_4 = \dots = E_i = E_L$$

and

(2.13)

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \frac{b_4}{a_4} = \dots = \frac{b_i}{a_i}$$

This is effectively saying that the properties of the second and higher layers with respect to evaporation and condensation are identical to those properties of the bulk liquid, for by E_L we refer to the heat of liquefaction of the adsorbate. If we use (2.13) and the definitions

$$x = \frac{a_i}{b_i} p e^{E_L/RT}, \quad i \neq 1$$

$$y = \frac{a_1}{b_1} p e^{E_L/RT} \quad (2.14)$$

we can write the equations (2.9) as

$$s_1 = y s_0$$

$$s_2 = x s_1 = c x^2 s_0$$

$$s_i = x s_{i-1} = c x^i s_0 \quad (2.9')$$

where $c = y/x$. When these are substituted into the series in (2.12) one is able to simplify the expression, the

denominator containing the sum of the infinite geometric series $\sum_{i=1}^{\infty} x^i$, and the numerator containing the product of x and the derivative of that series. Equation (2.12) becomes

$$\theta = \frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \quad (2.15)$$

One can see from the denominator of (2.15) that to satisfy the condition that the volume adsorbed at the saturation pressure be infinite, x must equal one. One has then

$$x = \frac{P}{P_o} \quad (2.16)$$

in general, and the substitution of (2.16) into (2.15) gives

$$\theta = \frac{v}{v_m} = \left(\frac{cP}{P_o - P} \right) \left\{ 1 + \left(c-1 \right) \frac{P}{P_o} \right\} \quad (2.15')$$

which is the final form of the BET " ∞ - form" isotherm.

Brunauer, Emmett, and Teller have also considered the case where adsorption, for some reason, is not possible beyond the n^{th} layer, rather than the possibility of an infinite number of layers as before. For this case the series in equation (2.10), (2.11) and thus (2.12) must be cut off at n . When this is done, rather than (2.15), one gets the following isotherm equation

$$\theta = \frac{v}{v_m} = \left(\frac{cx}{1-x} \right) \frac{(1-(n-1)x^n + nx^{n+1})}{1+(c-1)x - cx^{n+1}}, \quad (2.17)$$

which is known as the n-layer BET isotherm. It is interesting to note that if $n = 1$, (2.17) reduces to the Langmuir monolayer isotherm, and if $n \rightarrow \infty$, (2.17) becomes the same as (2.15), both of which results one would expect for this theory.

The BET theory has had very good success both in fitting experimental isotherms, and in calculating the heat of adsorption and the total surface area of an adsorbent from experimental isotherms. However the theory does have its shortcomings - mainly its neglect of lateral attraction between adsorbed molecules, and its assumption that molecules are adsorbed vertically on top of one another. We shall see that various workers have modified the theory in various ways to at least partially overcome these objections.

Halsey (25) has considered a modification in which second layer molecules are adsorbed onto the centre of a triangle of molecules in the first layer. His calculations show that unless the first layer is over $1/3$ filled, there will be very little filling of the second layer; and in any case there will be very little filling above the second layer unless the pressure is very close to saturation. We will consider Hill's modification, in which he includes lateral interactions, in the next section.

2.4 Multilayer Adsorption with Stepwise Isotherms

In 1947, Hill (26) gave a modified treatment of the BET theory in which he assumed that lateral interactions were present in all layers but were of sufficiently short range that those between nearest neighbours only need be considered. His work was actually to the BET theory, what Fowler's was to the Langmuir theory, for Hill used the Bragg-Williams approximation to calculate the effect of the lateral interactions. His assumption was that the molecules in the i^{th} layer, say n_i of them, serve as sites for the n_{i+1} molecules of the $(i + 1)^{\text{st}}$ layer, and that the n_i molecules are distributed randomly over the N sites of the lattice even though not all N sites are available to them. The n_{i+1} molecules of the next layer are distributed randomly over the n_i sites available to them, and hence are random over all N sites of the lattice. The number of nearest neighbour pairs in each layer is then calculated on the basis of this randomness and used in the partition function.

From the partition function Hill found n equations ($n = \text{number of layers}$) in n unknowns (the θ_i 's - the coverages of each layer). The final isotherm is the sum of the θ_i 's. Numerical methods had to be used to find solutions for the isotherm. From his calculations, Hill found isotherms which he says would indicate that for sufficiently large lateral

interactions and unrestricted adsorption ($n \rightarrow \infty$), steplike isotherms would result. Although he did not make calculations for the $n = \infty$ case, his isotherms for $n > 3$ and large interaction energies contained loops which when cut according to the rule of equal areas showed that each layer filled critically. In conclusion Hill noted that these results followed from a very crude approximation and that, although it does not happen in the monolayer case, the use of a higher order approximation or an exact method might change the qualitative nature of the isotherms.

Halsey and Champion (27) have extended Hill's treatment to include the transmission of energy from the adsorbent out to the n^{th} layer. E_1 is the energy of attraction between the first layer and the surface, and Halsey considers that this is transmitted outward, decaying with the cube of the distance from the surface, so that $E_n = E_1/n^3$ is the energy of attraction between the n^{th} layer and the surface. The effect of this is to spread the loops (i.e. the steps) of the isotherm on the horizontal scale. All of the steps occurred at the saturation pressure ($p = p_o$) in Hill's model, whereas in Halsey's model the first five steps occur at approximately $p = 0.28 p_o$, $p = 0.67 p_o$, $p = 0.86 p_o$, $p = 0.93 p_o$, and $p = 0.96 p_o$. The steps after the first three occur sufficiently close together that one would not expect to see them in an experimentally determined isotherm, even if the system were very nearly ideal. However the initial steps are very distinct.

The best example of an experimentally determined stepwise isotherm is the one reported by Singleton and Halsey (13). For the system krypton on carbon black which had been graphitized at 2700° K, the isotherm shows two very distinct steps in the region $1 < \theta < 2$ and $2 < \theta < 3$. It has been shown (14) that the adsorbent used had extremely large crystallites, and thus was very close to a uniform surface. The fact that most experimental systems yield smooth rather than step-like isotherms, together with calculations which show that the requirements necessary to remove the steps in his theory are entirely unphysical, is enough to make Halsey assert that a smooth isotherm is sufficient to conclude that the adsorbent in a system is far from uniform. The step-like isotherm is what one would expect in an ideal system.

For a more thorough review of these and other theories of adsorption, the reader is referred to the book by Young and Crowell (28).

Chapter 3. The Ising Model and Monolayer Adsorption

3.1 The Ising Model

In this chapter we will discuss the work of Ballentine and Betts (8,9) in which they apply the Ising model of ferromagnetism to the problem of localized monolayer adsorption.

When Ising (3) first proposed the model in 1925 he considered an ideal crystal of ferromagnetic material, and with each lattice point in the crystal he associated a spin variable σ_i which took on the discrete values +1 and -1 corresponding to "up" and "down" spin respectively. He neglected interactions between atoms in the lattice which were not nearest neighbours and he assumed that the n-n* atomic interaction could be expressed as $-J \sigma_i \sigma_j$, where i and j denote n-n spin sites. Thus the interaction energy of parallel spin pairs is $-J$, and that of antiparallel pairs is $+J$. The interaction of each spin with the external magnetic field is $-H \sigma_i$, where a spin $\sigma_i = +1$ is aligned in the direction of the magnetic field, and $\sigma_i = -1$ is aligned opposite to the field. The magnetic moment per spin has been set equal to one in the above definition. The total energy of the

*The abbreviation "n-n" will sometimes be used for "nearest neighbour."

ferromagnet is then

$$E = -J \sum_{\substack{n-n \\ \text{pairs}}} \sigma_i \sigma_j - H \sum_i \sigma_i , \quad (3.1)$$

and the partition function is

$$Z = \sum_{(\sigma_i)} \exp \left\{ \frac{J}{KT} \sum_{n-n} \sigma_i \sigma_j + \frac{H}{KT} \sum_i \sigma_i \right\} , \quad (3.2)$$

following Ballentine's notation where \sum represents the sum over all spin states $\sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1}$, for a lattice of N spins.

Ising himself was only able to solve the problem for the one-dimensional case. This system did not exhibit any critical behaviour so attention was turned to the two- and three-dimensional problems. Many workers found approximate solutions to the two-dimensional problem, all of which exhibited a finite jump in specific heat at some non-zero critical temperature (Curie point). The first exact result obtained for the two-dimensional problem came in 1941 when Kramers and Wannier (29) showed that the partition function could be derived by finding the largest eigenvalue of a matrix. For the simple quadratic lattice they found a unitary matrix transformation which established a symmetry relation between high and low temperature expressions for

the partition function. From this they deduced the location and nature of the singularity in the specific heat curve. An excellent review of this, and indeed of all the work done on the Ising model up to 1960, is found in a paper by Domb (30). Other good reviews of the Ising model are given by Newell and Montroll (31) and Hill (32). In 1963 Fisher (33) published a shorter but more up-to-date review of the problem.

In 1944 Onsager (34) succeeded in solving exactly the zero magnetic field case of the two-dimensional square lattice Ising model. To date neither the non-zero field nor the three-dimensional cases have been solved exactly. In 1949 Kaufman (35) simplified Onsager's matrix solution. In 1952 Kac and Ward (36) gave a combinatorial solution based on the counting of a certain type of graph on the appropriate lattice. Their solution was not completely justified until 1960 when Sherman (37) showed that their solution was equivalent to that of Onsager. In the meantime these various solutions had been extended to the triangular and hexagonal lattice cases. Yang (38) extended the matrix method to calculate the spontaneous magnetization of a simple quadratic ferromagnetic system, and this too was later extended to include the triangular and hexagonal lattice cases.

The most fruitful approach to the three-dimensional and non-zero field two-dimensional problems, for which no closed solutions have yet been found, is that of exact series expansions. Comparisons of the approximate methods with exact expansions have shown that the series method can always be made more accurate than any approximation without having to calculate an excessive number of terms. This and the fact that the approximations distort the results in the critical region, make the exact series approach a more profitable avenue to pursue, at least for the present.

Van der Waerden (39) and later Wakefield (40) used the combinatorial technique of graph counting to obtain the high temperature series expansion of the partition function for zero field. Their expansion coefficients involved the counting of closed graphs. Oguchi (41) derived a series for the zero-field magnetic susceptibility on a cubic lattice, which involved counting all graphs with two odd vertices. On the other hand Domb (42) used a matrix method to derive the series for the partition function on a simple quadratic lattice. Recently Domb and Sykes have done extensive work in extending the graph counting techniques. These techniques are described in detail in chapter 5 of the paper by Domb (30), and were used in calculating the series expansions which occur in Chapter 4 of this thesis.

3.2 Application to Localized Monolayer Adsorption with Lateral Interactions

In applying the Ising model to adsorption we consider the adsorbent to be a regular two-dimensional lattice, the vertices of which are all possible sites on which molecules of the adsorbate may settle. Thus each site may be in one of two states denoted as follows: $\sigma_i = +1$ if the site is occupied by an adsorbed molecule, and $\sigma_i = -1$ if the site is unoccupied. σ_i is now an "occupation" variable, although from time to time we may refer to it as "spin" in analogy to the ferromagnetic case. The subscript i simply refers to the lattice site and may take the values 1, 2, . . . , N. We can write the total number of adsorbed molecules as

$$N_a = \sum_i (1 + \sigma_i)/2 \quad (3.3)$$

and the total number of n-n pairs of adsorbed molecules as

$$N_p = \sum_{n-n} (1 + \sigma_i)(1 + \sigma_j)/4 \quad (3.4)$$

The model includes an attraction between every adsorbed molecule and the surface, characterized by an interaction energy $-E_s$, and an attraction between adsorbed n-n pairs, characterized by an interaction energy $-V$.

Including the chemical potential μ of the system the energy may be written as

$$E = -(\mu + E_s) N_a - V N_p . \quad (3.5)$$

Using (3.3), (3.4), and (3.5) the grand partition function of the adsorbed system is

$$Z = \sum_{(\sigma_i)} \exp \left\{ \frac{\mu + E_s}{2} \sum_i (1 + \sigma_i) + \frac{V}{4} \sum_{n-n} (1 + \sigma_i)(1 + \sigma_j) \right\}. \quad (3.6)$$

Expanding the product in the second term of (3.6) and remembering that there are $\frac{qN}{2}$ n-n pairs so that

$$\sum_{n-n} \sigma_i = \frac{q}{2} \sum_i \sigma_i , \quad (3.7)$$

we get

$$Z = \exp \left\{ \frac{N}{KT} \left(\frac{\mu}{2} + \frac{E_s}{2} + \frac{qV}{8} \right) \right\} \sum_{(\sigma_i)} \exp \left\{ \frac{(E_s + \mu + \frac{qV}{2})}{2KT} \sum_i \sigma_i + \frac{V}{4KT} \sum_{n-n} \sigma_i \sigma_j \right\} .$$

If we let $H = \frac{1}{2}(E_s + \mu + \frac{qV}{2})$ and $J = \frac{V}{4}$, then

$$Z = \exp \left\{ \frac{N}{KT} \left(\frac{\mu}{2} + \frac{E_s}{2} + \frac{qV}{8} \right) \right\} Z, \quad (3.8)$$

where Z is the standard Ising partition function of equation (3.2). The coefficient of Z in (3.8) is a function of temperature, but otherwise it is independent of the state of the adsorbed system.

3.3 Series Expansions of the Partition Function

We wish to have expansions of Z in both high and low temperature variables - i.e. variables which tend to zero as the temperature tends to infinity and zero respectively. For a given configuration of the system we say that of the N spins, n of them are "down" or negative spins, and of the $\frac{qN}{2}$ n-n pairs, m of them are antiparallel. Then we can write

$$\sum_i \sigma_i = N - 2n ,$$

and

$$\sum_{n-n} \sigma_i \sigma_j = \frac{qN}{2} - 2m .$$

Bringing the factors which are independent of the configuration of the system to the left of $\sum_{(\sigma_i)}$ we have

$$Z = \exp \left\{ \frac{NH}{KT} + \frac{qNJ}{2KT} \right\} \sum_{(\sigma_i)} \exp \left\{ -\frac{2nH}{KT} - \frac{2mJ}{KT} \right\} .$$

We now choose the variables

$$x = e^{-2J/KT} \quad \text{and} \quad y = e^{-2H/KT}, \quad (3.9)$$

noting that $x \rightarrow 0$ and $y \rightarrow 0$ as $T \rightarrow 0$. In the sum over states $\sum_{(\sigma_i)}$, the number of negative spins n will take on all values from 0 to N , and the number of antiparallel n-n spin pairs m will take on all values from

0 to q_n for a given n . Hence we can write

$$Z = x^{-\frac{qN}{2}} y^{-\frac{N}{2}} \sum_{n=0}^N \sum_{m=0}^{q_n} g(n, m; N) x^m y^n , \quad (3.10)$$

where $g(n, m; N)$ is the number of configurations on the lattice of n negative spins such that they form m anti-parallel spin pairs. Equation (3.10) is the low temperature (L.T.) expansion for Z , and the calculation of the actual series involves the counting of the configurations just described.

The high temperature (H.T.) series can be found by writing (3.2) in the form

$$Z = \sum_{(\sigma_i)} \prod_{n-n} e^{(J/KT) \sigma_i \sigma_j} \prod_i e^{(H/KT) \sigma_i} . \quad (3.11)$$

By expanding the exponential factors above, using the following relation

$$(\sigma_i)^2 = (\sigma_i \sigma_j)^2 = 1$$

and grouping the terms of the series properly, we can write

$$e^{\frac{J}{KT} \sigma_i \sigma_j} = (1 + \sigma_i \sigma_j u) \cosh \frac{J}{KT}$$

and

$$e^{\frac{H}{KT} \sigma_i} = (1 + \sigma_i v) \cosh \frac{H}{KT} \quad (3.12)$$

where $u = \tanh \frac{J}{KT}$ and $v = \tanh \frac{H}{KT}$. Substituting the relations (3.12) into equation (3.11) gives

$$Z = (\cosh \frac{J}{KT})^{\frac{qN}{2}} (\cosh \frac{H}{KT})^N \sum_{(\sigma_i)} \prod_{n-n} \prod_{i} (1 + \sigma_i \sigma_j u) \prod_i (1 + \sigma_i v). \quad (3.13)$$

We expand the products in (3.13) and consider the coefficient of $v^m u^\ell$. It will be the sum of all possible products of ℓ different factors of the form $\sigma_i \sigma_j$ and m different factors of the form σ_i . Each such product may be represented graphically if we let $\sigma_i \sigma_j$ be represented by a line or bond between the i^{th} and j^{th} sites on the lattice, and σ_k be represented by a circle around the k^{th} site. The coefficient of $v^m u^\ell$ then is represented by the sum of all the graphs of ℓ lines and m circles. However in the sum over states, if a particular term contains any factor σ_i to an odd power, its contribution will be zero. Hence graphs which contain only vertices which either are uncircled and are the meeting point of an even number of lines, or are circled and are the meeting point of an odd number of lines, will be the only ones to contribute to the final expansion. The form of the H.T. expansion for Z is

$$Z = (\cosh \frac{J}{KT})^{\frac{qN}{2}} (\cosh \frac{H}{KT})^N \sum_{\ell=0}^{\frac{qN}{2}} \sum_{m=0}^{2\ell} g(\ell, m; N) v^m u^\ell, \quad (3.14)$$

where $\mathcal{G}(\ell, m; N)$ is the number of graphs of ℓ lines which contain m odd vertices and can be drawn on a lattice of N sites. For large values of ℓ the upper limit of 2ℓ on m will never be realized, but for small ℓ a graph of ℓ lines will have at most 2ℓ vertices.

3.4 Calculations Using the Partition Function

Since we are considering a regular lattice, in which all sites must be identical, we will let the number of sites N become infinite, or consider the lattice boundaries to be cyclically connected. In this way we avoid any edge effects which might otherwise have entered.

However, we must first see how the partition function may be used to derive the physical quantities we are interested in. From statistical mechanics we know that we can find equilibrium values of a physical quantity by averaging that quantity over all the possible states of the system. For instance the internal energy of the ferromagnetic system has an equilibrium value given by

$$\bar{E} = \frac{\sum_s E_s e^{-E_s/KT}}{\sum_s e^{-E_s/KT}}, \quad (3.15)$$

where E_s refers to the energy of a particular state of the system, and \sum_s is the sum over states. From this it is

easy to show that the internal energy per spin is

$$\bar{E} = KT^2 \frac{\partial}{\partial T} \left(\frac{1}{N} \ln Z \right) . \quad (3.16)$$

The specific heat C_V is simply obtained by taking the derivative of \bar{E} with respect to T . The magnetization per spin can be found in a way analogous to (3.15) to be

$$\bar{M} = KT \frac{\partial}{\partial H} \left(\frac{1}{N} \ln Z \right) . \quad (3.17)$$

Ballentine has shown that the fractional coverage θ of the surface in the adsorption problem is related to \bar{M} by

$$\theta = \frac{1}{2} (\bar{M} + 1) . \quad (3.18)$$

If we remember how x , y , u , and v were defined in terms of J , H , and T we can write C_V and θ as functions of these variables.

Physically we know that $\lim_{N \rightarrow \infty} \frac{1}{N} \ln Z$ must be finite. Thus the series for $\ln Z$ must be independent of any powers of N greater than the first. Ballentine has rigorously derived the $\ln Z$ series from the series for Z , and used this condition on the coefficients of the $\ln Z$ series as a check of his work. It can be shown that the

coefficient of a given term in the $\ln Z$ series is simply the term linear in N in the polynomial coefficient of the corresponding term in the Z series. For example, in the H.T. Z series, the coefficients $\mathcal{G}(\ell, m; N)$ are polynomials in N , and the coefficient of the $v^m u^\ell$ term in the $\ln Z$ series is the term linear in N in $\mathcal{G}(\ell, m; N)$.

Using the series for $\frac{1}{N} \ln Z$, Ballentine has calculated the adsorption isotherms given by this model. For temperatures greater than a critical temperature T_c , the isotherms are smooth curves such that θ increases as the pressure increases. However for temperatures below T_c there is a finite discontinuity in the isotherm, occurring at a pressure P_o . Using the relation between the chemical potential μ and the pressure

$$e^{\frac{\mu}{KT}} = \left(\frac{h^2}{2\pi mKT} \right)^{\frac{3}{2}} \frac{P}{KT} \quad (3.19)$$

for an ideal gas (when the gas phase is in equilibrium with the adsorbed phase, the chemical potentials of the two phases are equal), one can show that this critical pressure P_o corresponds in this model to the case $H = 0$. Yang (38) has calculated an exact formula for the spontaneous magnetization (M when $H = 0$) of the simple quadratic Ising ferromagnet. Ballentine has used this formula to calculate exact

values for the isotherms right at the discontinuity. The critical temperature for this system on the simple quadratic lattice, first found by Kramers and Wannier (29) is given by

$$X_c = e^{-\frac{2J}{KT}c} = \sqrt{2} - 1 = 0.4142 . \quad (3.20)$$

3.5 Two or More Adsorbed Layers

Ballentine has also considered an extension of this model to treat two or more layers of adsorbed molecules. However this model is based on the physically unrealistic premise that the state of a site in a higher layer is independent of the states of the sites directly below it. This allows gas molecules to be adsorbed on top of holes in a lower layer. However, Ballentine studied this model because it was a simple picture of cooperative phenomena and still displayed a change in critical point with an increasing number of layers. Ballentine has shown that the treatment of the n-layer case for $2 < n < \infty$ is very difficult. For $n = 1, 2, \infty$ layers of a simple cubic lattice structure we are dealing with homogeneous lattices, each site having 4, 5, and 6 nearest neighbours respectively. However for any other value of n the lattices are inhomogeneous, sites in the top and bottom layers having five nearest neighbours while interior sites have six. Ballentine's method for calculating the series coefficients is not as successful for

inhomogeneous lattices as it is for homogeneous ones. He has, however, made an accurate calculation of the zero-field specific heat together with a good estimate of the critical temperature for the two-layer case. For the three and four layer cases he has made good calculations of the specific heat away from the critical region and has made rough estimates of the location of the critical point. For the limiting case of an infinite number of layers, the zero-field specific heat and the critical temperature can be found from Wakefield's (40,43) exact series expansion for the simple cubic lattice. Ballentine's results show that there is a smooth variation in critical temperature with the number of layers. This is shown in fig. 1, which is reproduced from Ballentine's thesis.

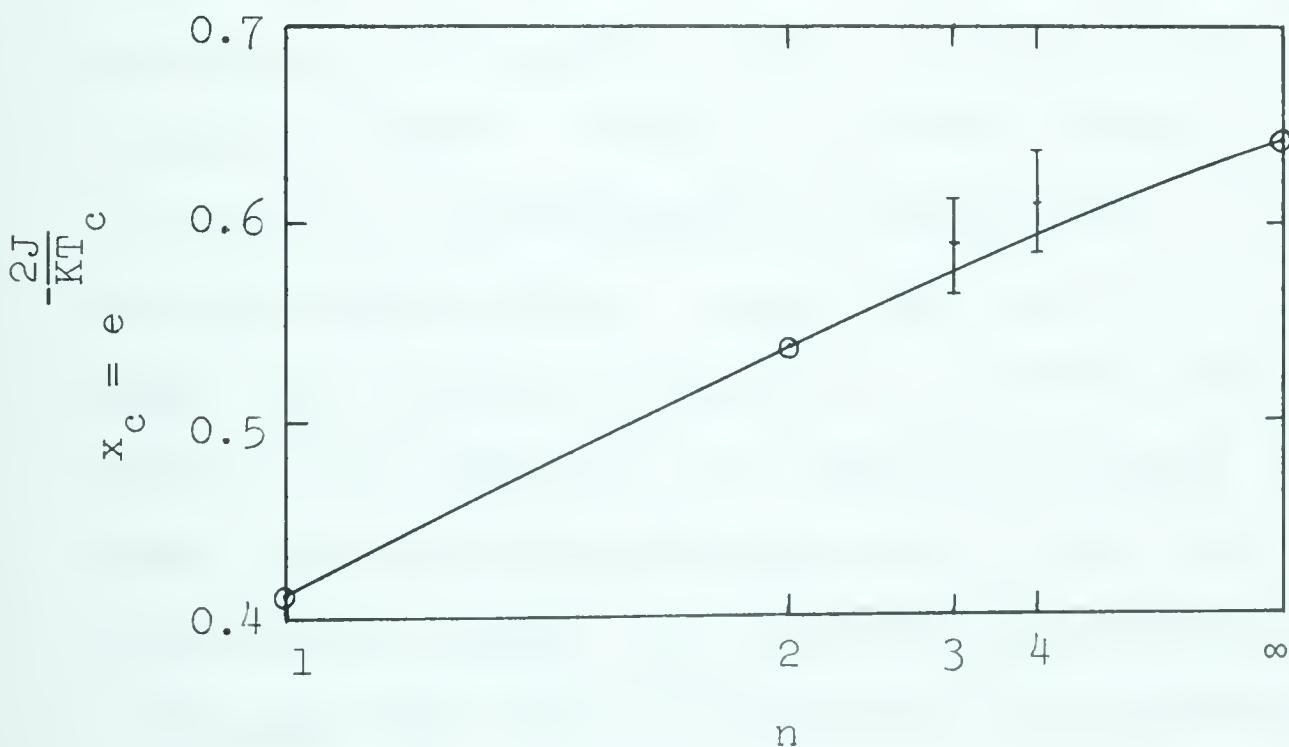


Fig. 1

The variation in critical point with the number of layers for the Ising model.

Chapter 4. The Model for Two-Layer Adsorption with Lateral Interactions

4.1 The Model

We saw in the last chapter that the two-layer Ising model when applied to adsorption permits the possibility of a second layer molecule being adsorbed on top of a hole or vacancy in the first layer. One of the principal reasons for suggesting a new model is to eliminate this unrealistic possibility. The model which we propose is as follows. We consider the adsorbent to be a two-dimensional square lattice of adsorption sites. Each site is capable of containing zero, one, or two adsorbed gas molecules. The first molecule on a given site is said to be in the first layer, and the second one in the second layer. To each site we assign an occupation ("spin") variable σ_i which takes on the values -1, 0, and +1 corresponding to occupancies of 0, 1, and 2 molecules respectively. We say that there is an interaction energy $-E_s$ between molecules in the first layer and the surface of the adsorbent, an interaction energy $-J_H$ between nearest neighbour pairs of molecules in the same layer, and an interaction energy $-J_V$ between two molecules adsorbed on the same site (and, by assumption, in different layers). We assume that all interactions are sufficiently short range that we may neglect all but n-n interactions.

This model should not be confused with the spin 1 Ising model for a ferromagnet composed of atoms with three atomic spin states. The interaction between molecules on the same site in the adsorption problem has no analogue in the ferromagnetic problem. Thus there will not be the same correspondence between the partition functions for the two cases that there was in Ballentine's work.

We can write the following expressions using the occupation variable σ_i :

$$\text{Number of molecules in first layer} = \sum_{i=1}^N \left(1 + \frac{\sigma_i(1 - \sigma_i)}{2} \right),$$

$$\text{Number of molecules in second layer} = \sum_i \left(\frac{\sigma_i(1 + \sigma_i)}{2} \right),$$

$$\text{Total number of molecules} = \sum_i (1 + \sigma_i). \quad (4.1)$$

Using the relations (4.1) we can write down the total energy of the adsorbed system.

$$E = -\mu \left[\sum_i (1 + \sigma_i) \right] - E_s \left[\sum_i \left(1 + \frac{\sigma_i(1 - \sigma_i)}{2} \right) \right] - J_H \sum_{n-n} \left[\left(1 + \frac{\sigma_i(1 - \sigma_i)}{2} \right) \left(1 + \frac{\sigma_j(1 - \sigma_j)}{2} \right) + \left(\frac{\sigma_i(1 + \sigma_i)}{2} \right) \left(\frac{\sigma_j(1 + \sigma_j)}{2} \right) \right] - J_V \left[\sum_i \left(\frac{\sigma_i(1 + \sigma_i)}{2} \right) \right]. \quad (4.2)$$

We expand this expression and use equation (3.7) to get the partition function Z .

$$Z = \sum_{(\sigma_i=0,\pm 1)} \exp \left\{ \frac{\mu N}{KT} + \frac{E_s N}{KT} + \frac{qJ_H N}{2KT} \right\} + \frac{J_H}{2KT} \sum_{n-n} (\sigma_i \sigma_j + \sigma_i^2 \sigma_j^2)$$

$$+ \left(\frac{\mu}{KT} + \frac{E_s}{2KT} + \frac{J_V}{2KT} + \frac{qJ_H}{2KT} \right) \sum_i \sigma_i + \left(\frac{-E_s}{2KT} + \frac{J_V}{2KT} - \frac{qJ_H}{2KT} \right) \sum_i \sigma_i^2 . \quad (4.3)$$

There are three parameters in this theory which are completely arbitrary: E_s , J_H , and J_V . However because (4.3) is so cumbersome and an expansion of it as it stands would be very difficult, we will simplify (4.3) by requiring that the coefficients of the $\sum_i \sigma_i$ and $\sum_i \sigma_i^2$ terms be zero.

$$J_V - E_s - q J_H = 0 ,$$

$$J_V + E_s + q J_H + 2\mu = 0 . \quad (4.4)$$

The first equation in (4.4) essentially restricts the physical systems to which we may apply the model as it now stands. The two equations (4.4) reduce the number of free interaction parameters from three to one and any system on which this is used must be such that the interactions are in the ratio which (4.4) requires. The presence of μ

in the second equation means (see equation (3.19)) that we have a fixed $p - T$ condition for this special case, and that we will be unable to calculate adsorption isotherms as long as (4.4) holds. The partition function, then, in which we are interested is

$$Z = \exp \left[\frac{N}{KT} (\mu + E_s + \frac{qJ_H}{2}) \right] \sum_{(\sigma_i=0, \pm 1)} \exp \left[\frac{J_H}{2KT} \sum_{n-n} (\sigma_i \sigma_j + \sigma_i^2 \sigma_j^2) \right]. \quad (4.5)$$

4.2 The low Temperature Series Expansion for Z

For the purpose of finding a L.T. expansion we write (4.5) as

$$Z = [A(T)]^N \sum_{(\sigma_i=0, \pm 1)} \prod_{n-n} \exp \left[\frac{J_H}{2KT} (\sigma_i \sigma_j + \sigma_i^2 \sigma_j^2) \right]. \quad (4.6)$$

We can see that the part of the energy of the adsorbed system which is dependent upon the configuration of the system, \mathcal{E} , is

$$\mathcal{E} = \sum_{n-n} \left[-\frac{J_H}{2} (\sigma_i \sigma_j + \sigma_i^2 \sigma_j^2) \right]. \quad (4.7)$$

By examining the possible values of the function $\sigma_i \sigma_j + \sigma_i^2 \sigma_j^2$ below

σ_i	-1	0	+1
σ_j			
-1	+2	0	0
0	0	0	0
+1	0	0	+2

$$f(\sigma_i, \sigma_j) = \sigma_i \sigma_j + \sigma_i^2 \sigma_j^2$$

we can see that \mathcal{E} will have its minimum value when either all "spins" are +1 or all are -1. The ground state is doubly degenerate and its energy is

$$\mathcal{E}_0 = -\frac{qN J_H}{2} .$$

For a higher energy state the configurational energy is incremented by J_H for every n-n pair of spins of type 0 (the pair (σ_i, σ_j) is type 0 or 2 depending upon whether $f(\sigma_i, \sigma_j) = 0$ or 2) which is introduced into the configuration.

The sum over states $\sum_{(\sigma_i=0, \pm 1)}$ includes every possible configuration of the system, so the L.T. expansion will start with the ground state, and each succeeding term will represent the successively higher energy states corresponding to the formation of more and more spin pairs of type 0. We choose the variable $x = e^{-J_H/KT}$, and write the L.T. series as

$$Z = [A(T)]^N \exp \left[\frac{qN J_H}{2kT} \right] \sum_{n=0}^{\frac{qN}{2}} 2g(n) x^n \quad (4.8)$$

$2g(n)$ is equal to the number of configurations on the lattice which contain n "spin" pairs of type 0. We have chosen to write this as $2g(n)$ because every configuration in which we are interested is related to one other similar configuration with the same energy which can be obtained by the transformation $(\begin{smallmatrix} +1 & \rightarrow & -1 \\ -1 & \rightarrow & +1 \end{smallmatrix})$. Thus in counting the configurations to evaluate $g(n)$ we agree to count only configurations which have a predominance of +1 "spins".

To aid in the counting of the configurations $g(n)$ we consider the following. In a given configuration of spins on the lattice we draw a line to separate each "spin" pair of type 0. These lines will form a "graph" on the reciprocal lattice. Since the lattice is cyclically connected all graphs will be closed. Hence to calculate $g(n)$ we must count all closed graphs of n bonds on the reciprocal lattice, the weight or contribution of each graph being the number of ways we can arrange +1, 0, and -1 spins in the interior of each lattice cell (the number of +1 "spins" must be greater than the number of -1 "spins") so that pairs of type 0 are always separated by a line and pairs of type 2 are not. Since the simple quadratic lattice is self-reciprocal we will be interested in closed graphs on a simple quadratic lattice.

Example: The separated closed configuration ($\boxed{\text{H}}$, $\boxed{\text{ }}\,$) of 13 bonds can be drawn on the s.q. lattice in $4N^2 - 60N$ ways. Each of these ways makes a contribution of 2, corresponding to the following ways of "filling" the graph:

$$\begin{array}{ccccccccc} + & + & + & + & + & + & + \\ + & \boxed{- - 0} & + & \boxed{0} & + \\ + & + & + & + & + & + & + \end{array}$$

$$\begin{array}{ccccccccc} + & + & + & + & + & + & + \\ + & \boxed{- - 0} & + & \boxed{-} & + \\ + & + & + & + & + & + & + \end{array}$$

Thus ($\boxed{\text{H}}$, $\boxed{\text{ }}\,$) makes a total contribution of $8 N^2 - 120 N$ to $g(13)$.

4.3 The High Temperature Series Expansion for Z

To make the H.T. series expansion we consider Z in the form (4.6) and expand the exponential term in $\sigma_i \sigma_j + \sigma_i^2 \sigma_j^2$ in an infinite series. We let

$$p_{ij} = \sigma_i \sigma_j + \sigma_i^2 \sigma_j^2 , \quad (4.9)$$

and we can easily prove that for the values $\sigma_i = 0, \pm 1$

$$\begin{aligned} p_{ij}^2 &= 2 p_{ij} \\ p_{ij}^n &= 2^{(n-1)} p_{ij} . \end{aligned} \quad (4.10)$$

The expansion becomes

$$Z = [A(T)]^N \sum_{(\sigma_i=0, \pm 1)} \prod_{n-n} \left\{ 1 + \frac{J_H}{2KT} p_{ij} + \frac{1}{2!} \left(\frac{J_H}{2KT} \right)^2 2p_{ij} + \frac{1}{3!} \left(\frac{J_H}{2KT} \right)^3 2^2 p_{ij} + \dots \right\}$$

Rearranging the terms we get

$$Z = [A(T)]^N \sum_{\substack{\sigma_i=0, \pm 1 \\ i}} \prod_{n-n} \left\{ 1 + \frac{p_{ij}}{2} \left[1 + \frac{J_H}{KT} + \frac{1}{2!} \left(\frac{J_H}{KT} \right)^2 + \frac{1}{3!} \left(\frac{J_H}{KT} \right)^3 + \dots \right] - \frac{p_{ij}}{2} \right\}$$

And finally

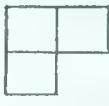
$$Z = [A(T)]^N \sum_{\substack{\sigma_i=0, \pm 1 \\ i}} \prod_{n-n} \left\{ 1 + p_{ij} \left(\frac{e^{\frac{J_H}{KT}} - 1}{2} \right) \right\}. \quad (4.11)$$

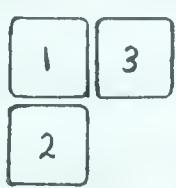
We choose the H.T. variable to be

$$w = \left(\frac{e^{\frac{J_H}{KT}} - 1}{2} \right) = \frac{1}{2} (x^{-1} - 1)$$

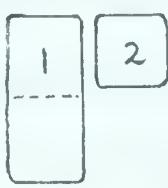
and note that as $T \rightarrow \infty$, $w \rightarrow 0$.

When we expand the product in (4.11) we note that the coefficient of w^n will be the sum of all possible products of $n p_{ij}$'s. We now associate with each p_{ij} a bond on the lattice drawn between the n - n sites i and j . Let us now consider the contribution that a given configuration of n bonds will make to the coefficient of w^n when we sum over all states of the system. The sum $\sum_{\sigma_k=0, \pm 1}$ will contribute a factor of 3 if the subscript k is absent from all the p_{ij} 's in the product (i.e., if no line goes through the k^{th} vertex of the lattice). Thus if m vertices have lines passing through them, the $N-m$ "empty" vertices will make a contribution of $e^{(N-m)}$ in the sum over states. The

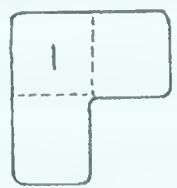
contribution from the m vertices which are touched by lines on the graph will be in two parts. A factor of 2 enters for each such vertex, and in addition a factor of 2 enters for each "irreducible loop" formed by the graph. By "loop" we mean a closed path, through all or part of a graph, around which one may travel and return to the starting point without retracing a step. By "irreducible loop" we mean the smallest loop which returns to a given starting point. An "irreducible loop" may have a boundary in common with another "irreducible loop" but it may not circumscribe any part of the area circumscribed by another one. For example the configuration  contains the three irreducible loops shown in fig. 2(a). The loops shown in figs. 2(b) - 2(d) for the same configuration are not all irreducible.



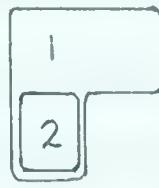
(a)



(b)



(c)



(d)

Fig. 2. (a) The three "irreducible loops" for the graph
 (b) & (c) - loop 1 is not a minimal path.
 (d) loop 1 circumscribes the whole area of loop 2.

If there are p irreducible loops in a given graph of n bonds, its total contribution to the coefficient of w^n in the sum over states will be $3^{(N-m)} 2^{(m+p)}$. The following relation for the p_{ij} 's

$$\sum_{\sigma_j=0, \pm 1} p_{ij} p_{jk} = 2 p_{ik} \quad (4.12)$$

together with (4.10) makes it easy to show that the above analysis is correct.

If we bring a factor 3^N outside the summations we can write the H.T. expansion for Z as

$$Z = [3A(T)]^N \sum_{n=0}^N \sum_{m=0}^{2n} \sum_p \left(\frac{2}{3}\right)^m 2^p G(n, m, (p); N) w^n, \quad (4.13)$$

where $G(n, m, (p); N)$ is the number of graphs of n bonds which touch m vertices and form p irreducible loops which can be drawn on a lattice of N sites. The counting of the graphs required for $G(n, m, (p); N)$ is quite laborious because all possible configurations of n bonds are involved and each configuration must further be classified according to the number of vertices it touches and the number of irreducible loops it includes before its contribution can be calculated. However, as we shall see in the next section these configurations have been counted and classified for small values of n .

4.4 The Calculation of the Various Series

As we have seen the calculation of the series coefficients for the two expansions involves the counting of graphs. This method has been used extensively by many

people working in the field of cooperative phenomena. Chapter 5 of the paper by Domb (30), written in collaboration with Sykes, gives a thorough treatment of the methods available to count virtually any type of graph. Most of the constants used to calculate the series coefficients were taken from the tables in Appendix 3 of Domb's paper. However the closed graphs of order greater than ten, i.e. of more than ten bonds, used in the L.T. series, and the separated graphs of order six used in the H.T. series were calculated particularly for this work. The equations and checks used in the calculation of the sixth order separated lattice constants are given the Appendix of this thesis.

Table 1 shows how the L.T. coefficients were calculated. Each contributing graph is listed together with the lattice constant for that configuration and the number of ways it can be "filled" according to the prescription in section 4.2. Table 2 provides a similar breakdown of the calculation of coefficients for the H.T. series for Z.

Table 1: Breakdown of the calculation of the low temperature series coefficients $g(n)$.

n No. of bonds	Configuration	Value latt. const.	Ways to fill	Configuration	Value latt. const.	Ways to fill	Coeff. of N in $g(n)$
4	; p_4	N	2				+2
6	; p_6	$2N$	1				+2
7	; p_{7a}	$2N$	3				+6
8	; p_8	$7N$	1	; p_{8h} and p_4, p_4	$\frac{N^2 - 5N}{2}$	4	-3
9	; p_{9k}	$12N$	1				+12
10	; p_{10}	$28N$	1		$4N$	5	
		$2N$	5	; p_{10a}	$8N$	2	
		$4N$	1	; p_6, p_4	$2N^2 - 24N$	2	+30
11	; p_{11}	$48N$	1		$4N$	1	
		$8N$	6	; p_{7a}, p_4	$2N^2 - 24N$	6	-44
12	; p_{12}	$124N$	1		$12N$	2	
		$6N$	1		$16N$	2	
		$12N$	1		$8N$	1	
		$32N$	1		N	7	

Table 1 (continued).

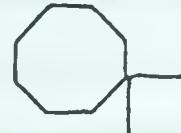
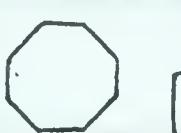
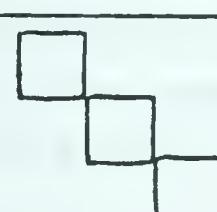
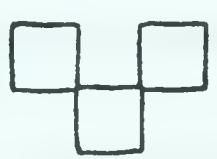
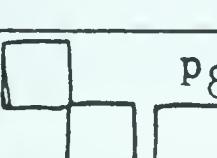
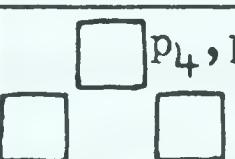
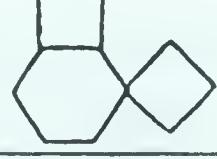
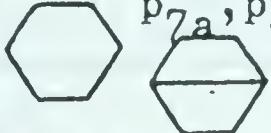
n No. of bonds	Configuration	Value latt. const.	Ways to fill	Configuration	Value latt. const.	Ways to fill	Coeff. of N in g(n)
12 cont.		32N	2	 p ₈ , p ₄	7N ² -106N	2	
		8N	1	 p ₆ , p ₆	2N ² -31N	1	
		2N	8		4N	8	
	 p _{8h} , p ₄	2N ² -28N	8	 p ₄ , p ₄ , p ₄	$\frac{1}{6}[4N^3 - 27N^2 + 194N]$	8	+ $\frac{470}{3}$
13		216N	1		2N	7	
		8N	7		4N	7	
		4N	7		20N	1	
		8N	1		8N	1	
		8N	1		8N	1	
		24N	2		24N	2	
		16N	2	 p _{9k} , p ₄	12N ² -180N	2	
		16N	3	 p _{7a} , p ₆	4N ² -62N	3	+44

Table 2: Breakdown of the calculation of the high temperature series coefficients $G(n,m,(p);N)$.

n	$G(n,m,(p);N)$	Lattice constants which contribute to $G(n,m,(p);N)$	Coeff. of N in $G(n,m,(p);N)$
1	$G(1,2,(0);N)$	(/)	+2
2	$G(2,3,(0);N)$	(\wedge)	+6
	$G(2,4,(0);N)$	(/,/)	-7
3	$G(3,4,(0);N)$	(\wedge\wedge), (\wedge\wedge)	+22
	$G(3,5,(0);N)$	(\wedge, /)	-60
	$G(3,6,(0);N)$	(/, /, /)	$+\frac{116}{3}$
4	$G(4,4,(1);N)$	(\square)	+1
	$G(4,5,(0);N)$	(X), (\wedge\wedge\wedge), (\wedge\wedge\wedge)	+87
	$G(4,6,(0);N)$	(\wedge\wedge, /), (\wedge\wedge, /), (\wedge\wedge, \wedge)	-406
	$G(4,7,(0);N)$	(\wedge, /, /)	+578
	$G(4,8,(0);N)$	(/, /, /, /)	$-\frac{521}{2}$
5	$G(5,5,(1);N)$	(\square\checkmark)	+8
	$G(5,6,(1);N)$	(\square, /)	-12
	$G(5,6,(0);N)$	(\wedge\wedge\wedge), (\wedge\wedge\wedge), (\wedge\wedge\wedge), (\wedge\wedge\wedge), (\wedge\wedge\wedge)	+364
	$G(5,7,(0);N)$	(\wedge\wedge\wedge, /), (\wedge\wedge\wedge, /), (X, /), (\wedge\wedge\wedge, /)	-2500

Table 2 (continued).

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n	$G(n, m, (p); N)$	Lattice constants which contribute to $G(n, m, (p); N)$	Coeff. of N in $G(n, m, (p); N)$
	$G(5, 8, (0); N)$	$(\nwarrow, /, /), (\nearrow, /, /), (\wedge, \wedge, /)$	+5822
	$G(5, 9, (0); N)$	$(\wedge, /, /, /)$	-5644
	$G(5, 10, (0); N)$	$(/, /, /, /, /)$	+ $\frac{9812}{5}$
6	$G(6, 6, (1); N)$	$(\text{hexagon}), (\square^\wedge), (\square^\nearrow), (\square^\nwarrow), (\square^\wedge)$	+54
	$G(6, 7, (1); N)$	$(\square^\wedge, /), (\square, \wedge)$	-168
	$G(6, 7, (0); N)$	$(\text{wavy}), (\text{wavy}), (\text{wavy}), (\text{X}^\vee)$	
		$(\text{X}^\wedge), (\text{V}), (\text{V}), (\text{Y}^\wedge), (\text{X}^\wedge)$	+1574
	$G(6, 8, (1); N)$	$(\square, /, /)$	+126
	$G(6, 8, (0); N)$	$(\text{wavy}, /), (\text{wavy}, /), (\text{X}^\wedge, /)$	
		$(\text{V}, /), (\text{X}^\wedge, /), (\text{wavy}, \wedge)$	
		$(\text{wavy}, \wedge), (\text{X}, \wedge), (\text{wavy}, \text{wavy})$	
		$(\text{wavy}, \wedge), (\wedge, \wedge)$	-14681
	$G(6, 9, (0); N)$	$(\text{wavy}, /, /), (\text{wavy}, /, /), (\text{X}, /, /)$	
		$(\text{wavy}, \wedge, /), (\wedge, \wedge, /), (\wedge, \wedge, \wedge)$	+49034
	$G(6, 10, (0); N)$	$(\text{wavy}, /, /, /), (\wedge, /, /, /)$	
		$(\wedge, \wedge, /, /)$	-76098
	$G(6, 11, (0); N)$	$(\wedge, /, /, /, /)$	+56040
	$G(6, 12, (0); N)$	$(/, /, /, /, /, /)$	- $\frac{47644}{3}$

As we said in Chapter 3 when discussing the monolayer case, since $\lim_{N \rightarrow \infty} (\frac{1}{N} \ln Z)$ exists physically we know that all powers of N greater than the first must cancel out when we convert from the Z series to the $\ln Z$ series. This was checked for the two-layer case, using the formulas for the series $\ln [f(x)]$ in terms of the series $f(x)$ which are given in Appendix I of Ballentine's thesis(8), and found to be correct. The coefficient of a power of x in the $\frac{1}{N} \ln Z$ series is simply the coefficient of N in the coefficient of the corresponding power of x in the Z series. We will now write down the L.T. and H.T. series for $\frac{1}{N} \ln Z$.

$$\text{L.T. } \frac{1}{N} \ln Z = \frac{\mu + E_s + q J_H}{KT} + \sum_{n=1}^{\infty} [\text{coeff. of } N \text{ in } g(n)] x^n + \frac{1}{N} \ln 2 . \quad (4.14)$$

Because of the conditions (4.4) the first term is zero, and in the limit $N \rightarrow \infty$ the last term becomes zero. Hence we have (using the results of Table 1)

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln Z = 2x^4 + 2x^6 + 6x^7 - 3x^8 + 12x^9 + 30x^{10} - 44x^{11} + \frac{470}{3}x^{12} + 44x^{13} + \dots \quad (4.15)$$

$$\text{H. T. } \frac{1}{N} \ln Z = \ln 3 + \frac{\mu + E_s + \frac{qJ_H}{2}}{KT} + \sum_{n=1}^{\infty} \left[\sum_m \sum_p \left(\frac{2}{3} \right)^m 2^p [\text{coeff. of } N \text{ in } G(n, m, (p); N)] \right] w^n, \quad (4.16)$$

and

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln Z = \ln 3 - \frac{2 J_H^2}{KT} + \frac{8}{9} w + \frac{32}{81} w^2 - \frac{352}{2187} w^3 - \frac{832}{6561} w^4 + \frac{5888}{295245} w^5 + \frac{397568}{1594323} w^6 + \dots \quad (4.17)$$

where we have set $q = 4$ and used (4.4) to simplify the second term.

We are interested in finding the singularity in the C_V curve so we must find the series for the free energy per site, \bar{E} , and the specific heat, C_V . Using the Boltzmann average one finds

$$\bar{E} = KT^2 \frac{d}{dT} \left(\frac{1}{N} \ln Z \right), \quad (4.18)$$

and of course we know

$$C_V = \frac{d\bar{E}}{dT} \quad (4.19)$$

It is desirable to express these quantities as derivatives with respect to the variable x and w . Using the definitions of these variables

$$x = e^{-J_H^2/KT} \quad \text{and} \quad w = \frac{1}{2} (e^{J_H^2/KT} - 1), \quad (4.20)$$

we get

$$\frac{d}{dT} = \frac{J_H}{K T^2} x \frac{d}{dx} \quad (4.21)$$

$$\frac{d}{dT} = - \frac{J_H}{K T^2} \left(w + \frac{1}{2} \right) \frac{d}{dw}. \quad (4.22)$$

Using (4.15) and (4.21) with (4.18) and (4.19) gives the following L.T. series:

$$\begin{aligned} \bar{E} = 2 J_H [& 4x^4 + 6x^6 + 21x^7 - 12x^8 + 54x^9 + 150x^{10} - 242x^{11} \\ & + 940x^{12} + 286x^{13} + \dots] , \end{aligned} \quad (4.23)$$

$$\begin{aligned} C_V = 2K (\ln x)^2 [& 16x^4 + 36x^6 + 147x^7 - 96x^8 + 486x^9 \\ & + 1500x^{10} - 2662x^{11} + 11280x^{12} + 3718x^{13} + \dots] . \end{aligned} \quad (4.24)$$

Equations (4.17), (4.18), (4.19), and (4.22) combine to give the H.T. series:

$$\bar{E} = 2 J_H \left[\frac{7}{9} - \frac{52}{81}w - \frac{200}{729}w^2 + \frac{2416}{6561}w^3 + \frac{13504}{59049}w^4 - \frac{225280}{531441}w^5 + \dots \right] \quad (4.25)$$

$$C_V = 4K [\ln(1+2w)]^2 \left[\frac{13}{81} + \frac{1002}{2187}w - \frac{12}{6561}w^2 - \frac{46120}{59049}w^3 + \frac{38528}{531441}w^4 + \dots \right]. \quad (4.26)$$

We note that due to the nature of the H.T. variable w we lose two terms in going from $\frac{1}{N} \ln Z$ to C_V in these latter series.

4.5 Estimation of the Critical Temperature - The Padé Approximant

The Padé (47) approximant is a rational approximation to a function which is represented by a power series.

To a given series $f(z) = \sum_n c_n z^n$ there corresponds a unique rational fraction $F_{N,M}(z)$, whose numerator is a polynomial in z of order M , and whose denominator is a polynomial of order N . When expanded in powers of z , $F_{N,M}(z)$ agrees term by term with the series $f(z)$ for more terms than any other rational fraction whose numerator and denominator are of degrees M and N respectively. The fraction $F_{N,M}(z)$, or as it is sometimes written $[N,M]$, is known as the Padé approximant to $f(z)$. For a proof that the Padé approximant is unique the reader is referred to a book on the subject of continued fractions such as Wall (44).

The approximant is of the form

$$[N,M] = F_{N,M}(z) = \frac{A_{N,M}(z)}{B_{N,M}(z)} = \frac{a_0 + a_1 z + a_2 z^2 + \dots + a_M z^M}{b_0 + b_1 z + b_2 z^2 + \dots + b_M z^M}. \quad (4.27)$$

The polynomials $A_{N,M}(z)$ and $B_{N,M}(z)$ are determined such that

$$f(z) B_{N,M}(z) - A_{N,M}(z) = (z^{N+M+1}), \quad (4.28)$$

where (z^{N+M+1}) represents a polynomial in z whose lowest term is z^{N+M+1} . One can satisfy (4.28) by taking the product

$$f(z)B_{N,M}(z) = c_0 b_0 + (c_0 b_1 + c_1 b_0) z + \\ (c_0 b_2 + c_1 b_1 + c_2 b_0) z^2 + \dots \quad (4.29)$$

and putting the coefficients of the terms in z^{M+r} , where $r = 1, 2, \dots, N$, equal to zero. A set of N equations in the $N+1$ unknowns b_0, b_1, \dots, b_N results and from this we can find b_1, b_2, \dots, b_N in terms of b_0 . We then set the first $M+1$ terms of the R.H.S. of (4.29) equal to $A_{N,M}(z)$. The coefficients a_0, a_1, \dots, a_M are all determined in terms of b_0 . The one unknown, b_0 , cancels out of the numerator and denominator, and we have thus determined the Padé approximant $F_{N,M}(z)$.

If the function $f(z)$ has a pole at some point z_c , then better and better approximations to z_c will be obtained by finding the zeros of $B_{N,N}(z)$ for larger and larger values of N . Baker (45) has used this method to estimate the critical point from the series expansions of the derivative of the magnetic susceptibility for the Ising model on various two and three-dimensional lattices. The results obtained by examining the poles of the sequence of $[N,N]$ approximants converge rapidly. For instance, for the simple quadratic lattice Baker gets $x_c = e^{-2J/KT} = 0.41421058$ from the approximant $[7,7]$, while x_c is known exactly to be $\sqrt{2} - 1 = 0.41421356 \dots$

We will now apply the Padé approximants to the L.T. and H.T. series for C_V and see if we can obtain an estimate of the location of the critical temperature. This will be the temperature at which the pole in the specific heat curve occurs. In table 3 below we have tabulated the denominator $B_{N,N}(x)$, and its real zero which corresponds to the pole in C_V , for the $[N,N]$ approximant to the L.T. C_V series.

$[N,N]$	Denominator $B_{N,N}(x)$ of $[N,N]$	x_c
$[1,1]$	$b_1 x$	0
$[2,2]$	$b_0(25,065 x^2 - 5,292 x + 1296)$	No real pole
$[3,3]$	$b_0(12.220504x^3 - 0.097543x^2 - 0.629173x - 1.000000)$	0.47647
$[4,4]$	$b_0(83.337721x^4 + 12.080791x^3 - 4.655109x^2 - 7.660339x - 1.000000)$	0.47968

Table 3. Results of the Padé Method on the L.T. C_V Series

Since we do not have enough terms in the series to calculate a higher order approximant we must base our estimate of x_c on the results above. After examining the trends in convergence in Baker's results, we feel quite safe in estimating the point of critical adsorption, correct to three figures, to be

$$x_c = e^{-J_H/KT} \simeq 0.479.$$

The H.T. series for C_V has been calculated up to only the fourth power in w . Hence the highest order approximant which can be found is [2,2]. Both [1,1] and [2,2] have been calculated, but unfortunately the pole for [1,1] is at a large negative value of w (which has no physical significance) and the poles for [2,2] are complex. To estimate the critical point from the H.T. series by the Padé method we would have to calculate at least four more terms in the series. The graph counting involved in such a calculation would be very laborious. It has not been done in this work.

4.6 The Ratio Method

The ratio method of estimating the singular point of a function represented by a power series has been used by Wakefield (43), Ballentine (8), and many others to estimate the critical point of various Ising model problems. If a series $\sum_n A_n$ converges, we know from the ratio test that the limit as $n \rightarrow \infty$ of $\frac{A_n}{A_{n-1}}$ must be less than one. If the series is a power series in u we can find the radius of convergence, which is characterized by the singular point closest to the origin, by taking the ratios of successive terms and extrapolating to find the limit as $n \rightarrow \infty$. We have

$$\lim_{n \rightarrow \infty} \left| \frac{a_n}{a_{n-1}} \right| = \frac{1}{u_c}, \quad (4.30)$$

where a_n is the coefficient of u^n in A_n and u_c is the critical point. The series converges for $|u| < u_c$. If we plot $\frac{a_n}{a_{n-1}}$ vs. $\frac{1}{n}$ and extend the graph to $n = \infty$, we can estimate u_c from the intercept of the graph using (4.30). In this method, one can also make use of the fact that if a function $f(u)$ has a pole at some critical point u_c , then successively higher powers of this function will have poles at this same point.

The L.T. C_V series was such that the signs of the terms were mixed positive and negative but were not alternating. Higher powers of the C_V series were taken until all terms became positive. However, when the ratios were plotted on the graph the points were far too irregular to make any extrapolation. The H.T. C_V series had so few terms that only three ratios could be found. It was felt that no reliable extrapolation could be made from so few points. The ratio method proved to be unsatisfactory for our series with the number of terms presently available.

Chapter 5. Discussion and Conclusion

5.1 Criticism of the Various Adsorption Theories

There are several criticisms that can be made of the various adsorption theories which we have looked at in Chapters II to IV. Apart from the other simplifying assumptions made, the monolayer theories may be criticized simply on the grounds that there are so few systems which exhibit the adsorption of only one layer. In the Langmuir theory all lateral interactions are neglected, when in fact we know that a molecule is affected by the presence or absence of molecules around it. The treatments of Fowler, Peierls, and Ballentine and Betts all include nearest neighbour lateral interactions and, although it can be shown that the effect of molecules beyond the nearest neighbours is small, there is bound to be some contribution from them. The first two of these theories use approximations (due to Bragg and Williams, and Bethe respectively) and are known to be in error in the critical region. Because the treatment due to Ballentine and Betts employs only exact methods, theirs is certainly the best localized monolayer theory to date. Some indication of the error involved in using the approximation is given in table 4, which compares the location of the critical point given by the two approximate methods with the exact location.

Method	$x_c = e^{-J/KT_c}$
Bragg-Williams Approx.	0.3679
Bethe Approx.	0.2501
Exact	0.1715

Table 4. Location of Critical Point as given by approximate and exact methods for the Ising Model.

Cernuschi's theory for two layer adsorption ignores all lateral interactions, while Dube's treats them in an approximate manner. However, both treatments implicitly assume that there is an interaction between the gas molecules in different layers, since the condition for critical adsorption is that the second layer molecules be more tightly bound than the first layer ones. A strong point of the Cernuschi and Dube theory is that the sites for molecules adsorbed into the second layer are formed by four molecules on the corners of a unit cell (square) in the first layer. This forms a close-packed structure which is the most logical way for adsorption to proceed.

The two fundamental objections to the BET theory are firstly that lateral interactions are neglected, and secondly that the molecules are adsorbed one on top of another, rather than in a close-packed structure. Hill's treatment was an

attempt to remedy the first point, although to do it he, too, used the Bragg-Williams approximation. Ballentine's many layer theory is good in that its treatment of lateral interactions is mathematically exact, but physically it only treats nearest neighbour contributions. However this theory is based on a rather unrealistic picture of adsorption which permits molecules to be adsorbed on top of holes in lower layers.

5.2 Summary

Several theories of adsorption, ranging from very elementary treatments of monolayer adsorption to more sophisticated treatments of multilayer adsorption, have been reviewed. The emphasis has been on localized adsorption although the mobile case has been considered. The simplifications and assumptions made in each theory have been discussed and the weaknesses of each have been criticized.

A model for localized two layer adsorption, in which the occupation of an adsorption site is considered to be one of three possible states for that site, has been presented. For this model we have had to take a special case to facilitate the expansion of the partition function of the system in both low and high temperature variables. The effect of this specialization has been to reduce the number of free interaction parameters from three to one. Series expansions for the partition function have been found

and the coefficients have been calculated using the graph counting techniques of Domb and Sykes. The expansions of \bar{E} , the free energy per site, and C_V , the configurational specific heat have been found from the partition function.

Two methods have been used in an attempt to estimate the location of the critical point of the two-layer adsorbed system. Only one method was successful. The specific heat curve has a pole at the critical point which will show up in the Padé approximant to C_V . The critical point is a singular point for both C_V and \bar{E} , so these two series will converge for $|x| < x_c$. In theory x_c could be estimated from these series using the ratio method. In fact this was not the case. For the H.T. series too few terms were known, and for the L.T. series the ratios were far too irregular to make any extrapolation.

An insufficient number of terms was known for the H.T. C_V series to make use of the Padé approximant. However, for the L.T. C_V expansion approximants up to the fourth order could be calculated. [3,3] indicated a pole at $x = 0.4765$, while [4,4] indicated a pole at $x = 0.4797$. On the basis of these results we feel safe in estimating x_c only to three figures. The estimate of the critical point of the two-layer adsorbed system which we give is $x_c = 0.479 \dots$.

To compare this result with the results obtained by Ballentine for the application of the Ising model to critical adsorption, we must note that the variable x as used by Ballentine is the square root of the x used in this thesis. Table 5 presents the locations of the critical point for these models.

Model	Location of critical point (x_c)
Ising - 1 layer	$x_c = 0.1716^*$
Ising - 2 layers	$x_c = 0.289$
Ising - ∞ layers	$x_c = 0.4119^{**}$
Present - 2 layers	$x_c = 0.479$

Table 5. Location of Critical Point for Ising and Present Models.

* Calculated by Kramers and Wannier (28)

** Calculated by Wakefield (39)

For a constant interaction energy, the critical temperature as predicted by the present model is much higher than that predicted by the 2 layer Ising model. We conclude that critical adsorption will take place in a system of gas molecules which have energies much higher than the cutoff one would expect from the Ising model.

5.3 Suggestions for Further Work

The best estimate of the critical point for this model is based on the fourth order Padé approximant which uses the first nine terms of the low temperature C_V expansion. If one could extend this series by an additional eight terms, the eighth order approximant could be used and the value of x_c found from this would be correct to about six figures. To do this would involve counting the closed configurations (both joined and separated) of up to and including 20 bonds. Considerable effort would be required but it is certainly feasible.

It is hoped that one could find an expansion of the partition function which would not require the simplifying restriction which has been placed on the interaction parameters. If this were possible the theory would be a completely general one with three parameters. We know from equation (3.17) that the pressure depends on the chemical potential μ . The restrictions given by equation (4.4) fix the value of μ and hence that of p . Thus to calculate theoretical isotherms for this model, it is necessary that we make the generalization and remove the restrictions (4.4). However, such an expansion will be very complicated because terms in $\Sigma\sigma_1$ and $\Sigma\sigma_1^2$ are involved.

The two layer theory was originally considered with the view that it would ultimately be extended to treat three or more layers, and possibly generalized to treat n layers. The extension to more layers would involve choosing an "occupation variable" with four or more possible states. This problem is suggestive of, but not the same as, the Ising model for particles of higher spin values. In this respect it is interesting to note that Betts (43) has recently developed a technique for treating nearest neighbour lattice problems where each element has four possible states. His techniques might well be applied to the three layer adsorption problem.

We conclude by noting that the model which has been proposed in this thesis and which we have suggested might be extended to include more layers, is an improvement over the Ising model for several layers as far as the structure of the adsorbed phase is concerned. However, it may still be criticized on the grounds that one would expect the adsorbed phase to have a close-packed lattice structure. In this respect the model cannot be improved because of its inherent two-dimensional nature.

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APPENDIXCALCULATION OF THE SEPARATED LATTICE CONSTANTS OF SIX BONDS

As a check of the calculation two equations are given for each constant but the last one. A check for this one is provided by the fact that the total number of configurations of six bonds must be $\binom{2N}{6}$.

$$\text{A. } (\square, /) = (\square)(/) - 5(\square) - 2(\square^{\diagdown}) - (\square^{\wedge}) - 2(\square^{\leftarrow}) \\ = 2(\square) = 16N^2 - 120N$$

$$(\square, /) = 8(\square, /) - (\square^{\wedge}) = 16N^2 - 120N$$

$$\text{B. } (\square, \wedge) = (\square)(\wedge) - 8(\square) - 2(\square^{\diagdown}) - (\square^{\wedge}) = 6N^2 - 48N$$

$$(\square, \wedge) = \frac{1}{2} [6(\square, /) - (\square^{\wedge})] = 6N^2 - 48N$$

$$\text{C. } (\times, /) = (\times)(/) - 5(\times) - (\times^{\wedge}) - 2(\times^{\leftarrow}) \\ = 2(\times) = 24N^2 - 220N$$

$$(\times, /) = 12(\times, /) - (\times^{\wedge}) = 24N^2 - 220N$$

$$\text{D. } (\times, \wedge) = (\times)(\wedge) - 6(\times) - (\times^{\wedge}) - (\times^{\leftarrow}) \\ = (\times^{\leftarrow}) = 6N^2 - 62N$$

$$(\times, \wedge) = \frac{1}{2} [6(\times, /) - (\times^{\wedge})] = 6N^2 - 62N$$

$$\text{E. } (\wedge, \wedge) = \frac{1}{2} (\wedge)(\wedge) - (\wedge) - 12(\times) - 2(\times^{\leftarrow}) - 2(\times^{\wedge}) \\ = 2(\square) - 2(\times^{\leftarrow}) = 8N^2 - 84N$$

$$(\wedge, \wedge) = \frac{1}{6} [2(\wedge, \wedge) - 2(\times^{\wedge}) - (\times^{\leftarrow})] = 8N^2 - 84N$$

$$\text{F. } (\sim\!\!\sim\!\!\sim, /) = (\sim\!\!\sim\!\!\sim)(/) - 5(\sim\!\!\sim\!\!\sim) - 2(\sim\!\!\sim\!\!\sim\sim) - 2(\sim\!\!\sim\!\!\sim\leftarrow) \\ = (\sim\!\!\sim\!\!\sim) - 6(\square) - 2(\square^{\wedge}) - (\square^{\leftarrow}) \\ = 284N^2 - 2622N$$

$$(\sim\!\!\sim\!\!\sim, /) = \frac{1}{2} [6(\sim\!\!\sim\!\!\sim, /) - 2(\square, /) - 2(\sim\!\!\sim\!\!\sim\sim)] \\ = 284N^2 - 2622N$$

G. $(\times, /) = (\times)(/) - 5(\times\times) - 3(\times\checkmark) - (\square') - (\checkmark\checkmark)$
 $= 36N^2 - 326N$

H. $(\times, /) = \frac{1}{2} [2(\wedge\wedge, /) - (\checkmark\checkmark)] = 36N^2 - 326N$

I. $(\wedge\wedge, /) = (\wedge\wedge)(/) - 5(\wedge\wedge) - (\wedge\wedge\wedge) - 4(\times\wedge)$
 $- (\checkmark\checkmark) - 3(\times\wedge) - 2(\square') - 4(\checkmark) - (\wedge\wedge)$
 $= 184N^2 - 1708N$

$(\wedge\wedge, /) = 3(\wedge\wedge, /) - 2(\square', /) - (\wedge\wedge\wedge) = 184N^2 - 1708N$

J. $(\wedge\wedge, /) = (\wedge\wedge)(/) - 5(\wedge\wedge) - (\wedge\wedge) - 2(\checkmark\checkmark) - 2(\times\wedge)$
 $- 3(\checkmark\checkmark) - 2(\square') - 2(\square') = 200N^2 - 1820N$

$(\wedge\wedge, /) = \frac{1}{2} [6(\wedge\wedge, /) - (\wedge\wedge) - 2(\square', /)] = 200N^2 - 1820N$

K. $(\wedge\wedge, \wedge) = (\wedge\wedge)(\wedge) - 4(\wedge\wedge) - 9(\times\wedge) - 2(\checkmark\wedge) - 8(\times\times)$
 $- (\wedge\wedge) - (\wedge\wedge\wedge) - 2(\checkmark\wedge) - 2(\times\wedge) - (\wedge\wedge)$
 $- (\square') - 4(\square') - 2(\times\wedge) - 3(\times\times) - 4(\square') - 2(\square') - 4(\checkmark) = 216N^2 - 2216N$

$(\wedge\wedge, \wedge) = \frac{1}{2} [6(\wedge\wedge, /) - (\wedge\wedge) - 2(\times\wedge) - (\checkmark\wedge)$
 $- (\wedge\wedge\wedge)] = 216N^2 - 2216N$

L. $(\wedge\wedge, \wedge) = (\wedge\wedge)(\wedge) - 3(\wedge\wedge) - 2(\wedge\wedge\wedge) - 2(\wedge\wedge\wedge)$
 $- 4(\wedge\wedge\wedge) - 2(\checkmark\wedge) - (\wedge\wedge) - 3(\checkmark\wedge) - 3(\times\wedge)$
 $- (\wedge\wedge\wedge) - (\times\wedge) - 6(\square') - 2(\square') - 2(\checkmark)$
 $- 4(\square') - 2(\square') - 6(\checkmark) = 300N^2 - 3128N$

$(\wedge\wedge, \wedge) = \frac{1}{2} [6(\wedge\wedge, /) - 2(\wedge\wedge\wedge) - (\wedge\wedge) - 3(\checkmark\wedge)]$
 $= 300N^2 - 3128N$

M. $(\wedge\wedge, \wedge) = \frac{1}{2} [(\wedge\wedge)(\wedge\wedge) - (\wedge\wedge) - 2(\wedge\wedge) - 2(\wedge\wedge\wedge)$
 $- 2(\wedge\wedge\wedge) - 2(\wedge\wedge) - 6(\wedge\wedge) - 4(\times\wedge)$
 $- 10(\square') - 4(\times\times) - 2(\square') - 4(\checkmark) - 4(\square') - 4(\square')$
 $- 4(\square') - 2(\wedge\wedge) - 12(\square) - 6(\checkmark)]$
 $= 162N^2 - 1723N$

N. $(\wedge\wedge, \wedge) = \frac{1}{2} [6(\wedge\wedge, \wedge) - 2(\wedge\wedge\wedge) - (\wedge\wedge)] = 162N^2 - 1723N$

$$\begin{aligned}
 \text{M. } (\wedge, \wedge) &= (\wedge)(\wedge) - 2(\wedge \wedge) - (\wedge \wedge) - (\wedge \wedge \wedge) - (\wedge \wedge \wedge) \\
 &\quad - 6(\wedge \wedge) - (\wedge \wedge \wedge) - 2(\square) - 2(\square) - 2(\square) \\
 &= 72N^2 - 772N
 \end{aligned}$$

$$(\wedge, \wedge) = \frac{1}{2} [6(\wedge, \wedge) - (\wedge \wedge \wedge) - (\wedge \wedge \wedge)] = 72N^2 - 772N$$

$$\begin{aligned}
 \text{N. } (\square, /, /) &= \frac{1}{2} [(\square, /)(/) - 5(\square, /) - (\square, /) - 2(\square, \wedge) \\
 &\quad - (\square \wedge)] = 2N^3 - 31N^2 + 126N
 \end{aligned}$$

$$\begin{aligned}
 (\square, /, /) &= (/)(\square) - 2(\square) - (\square) - (\square) - 2(\square) \\
 &\quad - 4(\square, /) - (\square, /) = 2N^3 - 31N^2 + 126N
 \end{aligned}$$

$$\begin{aligned}
 \text{o. } (\wedge \wedge, /, /) &= \frac{1}{2} [(\wedge \wedge, /)(/) - 5(\wedge \wedge, /) - 2(\wedge \wedge, /) \\
 &\quad - 2(\wedge \wedge \wedge, /) - (\wedge \wedge, /) - 2(\wedge \wedge, \wedge) - (\wedge \wedge) \\
 &\quad - 2(\wedge \wedge \wedge) - 3(\wedge \wedge) - 2(\square, /)] \\
 &= 100N^3 - 1918N^2 + 9672N
 \end{aligned}$$

$$\begin{aligned}
 (\wedge \wedge, /, /) &= \frac{1}{2} [6(\wedge, /, /) - 8(\square, /, /) - 2(\wedge \wedge, /)] \\
 &= 100N^3 - 1918N^2 + 9672N
 \end{aligned}$$

$$\begin{aligned}
 \text{p. } (\wedge \wedge, /, /) &= \frac{1}{2} [(\wedge \wedge, /)(/) - 5(\wedge \wedge, /) - (\wedge \wedge \wedge, /) - (\wedge \wedge) \\
 &\quad - 4(\wedge \wedge, /) - 3(\wedge \wedge, /) - 2(\wedge \wedge, /) - 2(\wedge \wedge, \wedge) \\
 &\quad - 2(\wedge \wedge) - (\wedge \wedge) - (\wedge \wedge \wedge) - 2(\square, /)] \\
 &= 72N^3 - 1372N^2 + 6856N
 \end{aligned}$$

$$(\wedge \wedge, /, /) = \frac{1}{2} [4(\wedge, /, /) - 2(\wedge \wedge, /)] = 72N^3 - 1372N^2 + 6856N$$

$$\begin{aligned}
 \text{q. } (\times, /, /) &= \frac{1}{2} [(\times, /)(/) - 5(\times, /) - (\times, /) - 2(\times, \wedge) \\
 &\quad - (\times \wedge)] = 2N^3 - 39N^2 + 198N
 \end{aligned}$$

$$(\times, /, /) = \frac{1}{4} [(\wedge, /, /) - (\times, /, /)] = 2N^3 - 39N^2 + 198N$$

$$\begin{aligned}
 \text{R. } (\wedge, \wedge, /) &= (\wedge, \wedge)(/) - 5(\wedge, \wedge) - 2(\wedge \wedge, \wedge) - (\wedge \wedge) \\
 &\quad - 2(\wedge \wedge, \wedge) - 4(\wedge, \wedge) - 3(\wedge, \wedge) - (\wedge \wedge) \\
 &\quad - 4(\square, \wedge) - 2(\wedge \wedge \wedge) - (\wedge \wedge \wedge) \\
 &= 216N^3 - 4324N^2 + 22996N
 \end{aligned}$$

$$\begin{aligned}
 (\wedge, \wedge, /) &= \frac{1}{2} [12(\wedge, /, /) - 4(\wedge, \wedge) - 2(\wedge \wedge, /) \\
 &\quad - 2(\wedge \wedge, /)] = 216N^3 - 4324N^2 + 22996N
 \end{aligned}$$

S. $(\wedge, \wedge, /) = (\wedge, \wedge)(/) - 5(\wedge, \wedge) - 4(\times, \wedge) - (\nwarrow, \wedge)$
 $- 2(\wedge, \nwarrow) - 6(\wedge, \wedge) - (\times^{\vee}) - (\wedge \nwarrow)$
 $- (\rightarrow \times) - 2(\times \times) = 48N^3 - 968N^2 + 5168N$

$(\wedge, \wedge, /) = \frac{1}{2} [12(\wedge, /, /) - 2(\wedge, \nwarrow) - (\nwarrow \nwarrow, /)$
 $- (\times^{\vee}, /)] = 48N^3 - 968N^2 + 5168N$

T. $(\wedge, \wedge, \wedge) = \frac{1}{3} [(\wedge, \wedge)(\wedge) - 2(\wedge, \wedge) - 2(\nwarrow, \wedge) - (\nwarrow \wedge)$
 $- 2(\nwarrow \nwarrow, \wedge) - 6(\wedge, \wedge) - 6(\times, \wedge) - 2(\nwarrow \nwarrow, \wedge)$
 $- 4(\square, \wedge) - 2(\nwarrow \nwarrow) - (\nwarrow \nwarrow) - 3(\nwarrow \nwarrow)$
 $- (\wedge \nwarrow) - (\nwarrow \wedge) - 3(\times^{\vee}) - 3(\rightarrow \times) - (\square^{\wedge})$
 $- 4(\times \times) - (\square^{\wedge}) - (\times \times)]$
 $= 36N^3 - 744N^2 + 4144N$

$(\wedge, \wedge, \wedge) = \frac{1}{6} [6(\wedge, \wedge, /) - 2(\nwarrow \nwarrow, \wedge) - (\nwarrow \nwarrow, \wedge)]$
 $= 36N^3 - 744N^2 + 4144N$

U. $(\nwarrow, /, /, /) = \frac{1}{3} [(\nwarrow, /, /)(/) - 5(\nwarrow, /, /) - 2(\nwarrow \nwarrow, /, /)$
 $- 2(\nwarrow \nwarrow, /) - 2(\nwarrow, \nwarrow) - 2(\nwarrow, \wedge, /)$
 $- 2(\nwarrow \nwarrow, \wedge, /) - 2(\nwarrow \wedge, /) - 4(\square, /, /)]$
 $= 24N^4 - 712N^3 + 7342N^2 - 26604N$

$(\nwarrow, /, /, /) = \frac{1}{2} [6(\wedge, /, /, /) - 2(\nwarrow \nwarrow, /, /)]$
 $= 24N^4 - 712N^3 + 7342N^2 - 26604N$

V. $(\wedge, /, /, /) = \frac{1}{3} [(\wedge, /, /)(/) - 5(\wedge, /, /) - 4(\times, /, /)$
 $- 2(\wedge, \wedge, /) - (\wedge, \nwarrow) - (\nwarrow \nwarrow, /) - (\times^{\vee}, /)$
 $- (\nwarrow \nwarrow, /)] = \frac{16}{3}N^4 - 160N^3 + \frac{4988}{3}N^2 - 6048N$

$(\wedge, /, /, /) = \frac{1}{3} [2(\wedge, /, /, /) - (\nwarrow \nwarrow, /, /)]$
 $= \frac{16}{3}N^4 - 160N^3 + \frac{4988}{3}N^2 - 6048N$

W. $(\wedge, \wedge, /, /) = \frac{1}{4} [18(\wedge, /, /, /) - 2(\nwarrow \nwarrow, /, /) - (\nwarrow \nwarrow, /, /)$
 $- 2(\nwarrow, \wedge, /)] = 36N^4 - 1094N^3 + 11600N^2 - 43446N$

$$\begin{aligned}
 (\wedge, \wedge, /, /) &= \frac{1}{2} [(\wedge, \wedge, /)(/) - 5(\wedge, \wedge, /) - 2(\nwarrow, \wedge, /) \\
 &\quad - 3(\wedge, \wedge, /) - 6(\wedge, \wedge, \wedge) - (\nwarrow \nwarrow, /) \\
 &\quad - 2(\nwarrow \nwarrow, \wedge) - (\nwarrow \nwarrow, /) - (\nwarrow \nwarrow, \wedge)] \\
 &\approx 36N^4 - 1094N^3 + 11600N^2 - 43446N
 \end{aligned}$$

$$\begin{aligned}
 \text{X. } (\wedge, /, /, /, /) &= \frac{1}{4} [(\wedge, /, /, /)(/) - 5(\wedge, /, /, /) - 3(\wedge, /, /, /) \\
 &\quad - 2(\nwarrow, /, /, /) - 4(\wedge, \wedge, /, /) - 2(\nwarrow \nwarrow, /, /) \\
 &\quad - (\nwarrow \nwarrow, /, /) - (\nwarrow \nwarrow, /)] \\
 &\approx 4N^5 - 164N^4 + 2607N^3 - 19217N^2 + 56040N
 \end{aligned}$$

$$\begin{aligned}
 (\wedge, /, /, /, /) &= \frac{1}{2} [30(/, /, /, /, /) - 2(\nwarrow, /, /, /)] \\
 &\approx 4N^5 - 164N^4 + 2607N^3 - 19217N^2 + 56040N
 \end{aligned}$$

$$\begin{aligned}
 \text{Y. } (/, /, /, /, /) &= \frac{1}{6} [(/, /, /, /, /)(/) - 5(/, /, /, /, /) \\
 &\quad - 2(\wedge, /, /, /, /) - (\nwarrow, /, /, /)] \\
 &\approx \frac{4}{45}N^6 - \frac{14}{3}N^5 + \frac{905}{9}N^4 - \frac{2239}{2}N^3 + \frac{584627}{90}N^2 - \frac{47644}{3}N
 \end{aligned}$$

Final Check:

Total connected constants of six bonds = 1628N

Total separated constants of six bonds

$$= \frac{4}{45}N^6 - \frac{2}{3}N^5 + \frac{17}{9}N^4 - \frac{5}{2}N^3 + \frac{137}{90}N^2 - \frac{4885}{3}N$$

Total number of configurations of six bonds = $\binom{2N}{6}$.

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